Adjustment of Temperature Scale of Cox Charts

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The value of C used in preparing the temperature scale of a Cox chart laid off according to the equation $y = \alpha t/(t + C)$ can be adjusted to any chosen value by adding or subtracting the appropriate number for each temperature on the calibrated scale. Thus any one type of ruled Cox chart paper can easily be adapted to give straight lines for the temperature–vapor pressure relationship of any type of compound. This also constitutes a convenient graphical method for evaluating C in the Antoine equation, $\log P = A - B/(t + C)$.

THE Cox chart (*3*), as developed by Davis (*4*) and Calingaert and Davis (*2*), offers the most convenient way of recording and using data on the relation of vapor pressure to temperature. Since this relationship for a given compound is represented by a straight line on the Cox chart, reliable interpolations and extrapolations are readily made. Also, the reliability of the experimentally determined points can be estimated from the magnitude of the random deviations of the points from the straight line.

As generally used, the Cox chart presents a graphical representation of the Antoine (*1*) equation

$$\log_{10} P = A - B/(t + C) \qquad (1)$$

where P = pressure in mm., $t = °$ C., and A, B, and C are constants. For the usual set of simplifying assumptions, $C = 273$, and the term $(t + C)$ becomes T in $°$ K. In practice, it is found

that C is usually less than 273 and varies for different families of compounds, and even for members of the same family. In his excellent review on the Antoine equation, Thomson (6) showed that in a homologous series the proper value of C was different for each compound and decreased with increasing boiling point. [Dreisbach and Spencer (5) stated that C increases with increasing boiling point; probably this was a typographical error.]

In most work, not of the highest precision, C is taken as 230, this being an average value, which is reasonably satisfactory when the data are not highly accurate or when only limited ranges of pressure are to be covered. Most commercially available Cox chart paper also uses $C = 230$, although some use $C = 273$. Since, in most cases, neither value of C is correct, a simple method of determining the proper value of C is needed. Thomson (6) described several methods, all of which are more or less laborious. In the use of Cox charts, the knowledge of the proper value of C is worthless unless one has, or is willing to prepare, a chart with a temperature scale based on that value of C. Since the calculation, graduation, and ruling of such a chart is laborious, the usual practice is to use the available paper, even though the lines determined by the data may be curved instead of straight.

In recent years, scores of derivatives of lactic acid, mostly esters, have been prepared in this laboratory. In correlating vapor pressure–temperature data on these compounds, a simple way was found for converting commercial Cox chart paper having the temperature scale based on $1/(t + 273)$ to a scale $1/(t + k)$. This transformation consisted of adding $273 - k$ to each temperature on the scale. Thus, if a scale $1/(t + 233)$ is desired, $40°$ $(273 - 233 = 40)$ should be added to every numerical value on the original temperature scale. The original rulings are thus retained. To determine the proper value of k, a trial and error method is used. When the value of k is high, the resulting line is convex upward; when k is too low, the line is concave upward. Usually two or three trials are sufficient, and these can be made for a single compound in a few minutes.

A reviewer has pointed out that the transformation here discussed is apparent from the consideration that since the temperature scale is a linear function of $1/(t + C)$, addition of any quantity to t is equivalent to subtracting that quantity from C.

The mathematical proof of the identity of C in Antoine's equation and k as determined above is as follows: In the graduation of the temperature scale of a Cox chart (on which a pressure-temperature line is a graphical form of the Antoine equation), the zero point is taken as $0°$ C., and distances, y, in suitable units, are measured according to the equation

$$ y = \frac{at}{t + 273} $$

where a is a constant.

If now, we add $n°$ to every point on the scale (that

is, $0°$ becomes $n°$, $50°$ becomes $50 + n°$, etc.), the equation of the new scale is $y = \frac{a(t' - n)}{t' + 273 - n}$, where $t' = t + n$. The point of reference, where $y = 0$, is still at the point where $t = 0$ and $t' = n$. Now let $t' = 0$. Then $y = \frac{-an}{273 - n}$. Since the point of reference is to be moved to the point $t' = 0$, let y be replaced by y' such that

$$ y' = y + \frac{an}{273 - n}. \quad \text{Then} $$

$$ y' - \frac{an}{273 - n} = $$

$$ \frac{a(t' - n)}{t' + 273 - n}. $$

Simplifying and collecting terms, this gives

$$ y' = $$

$$ \frac{273a}{273 - n}\left(\frac{t'}{t' + 273 - n}\right) = $$

$$ \frac{a't'}{t' + 273 - n} $$

Comparing this with the original equation, $\frac{at}{t + 273}$, we see that the two are of the same form except that the value of the constant, C, has been changed from 273 to $273 - n$. An incidental result is that the actual size of each degree interval on the chart has been increased. Thus points can be located with greater precision. This is especially advantageous when working with high boiling compounds. Another useful result is that the upper limit of the temperature scale has been raised by $n°$.

Obviously, similar relationships hold with charts graduated according to $y = \frac{at}{t + 230}$. Addition of $n°$ to each temperature is equivalent to subtracting n from 230, and the new equation is $y' = \frac{a't'}{t' + 230 - n}$. Similarly, one may convert a temperature scale based on any value of C to one based on any other desired value.

Figure 1 illustrates the use of the transformation described. Boiling points of n-octyl lactate were determined over the range 0.025 to 760 mm. and plotted on a Cox chart, the temperature scale of which was linear with $1/(t + 273)$. The result showed a distinct curvature (the line was drawn straight to show clearly the curvature of the points). The scale was then transformed to $1/(t + 183)$ by adding $90°$ to each temperature on the original scale. The boiling points plotted on the new scale were very nearly in a straight line. It should be noticed also that the temperature scale was expanded and its limits raised by the transformation.

Figure 1. Vapor Pressure–Temperature Chart for n-Octyl Lactate

LITERATURE CITED

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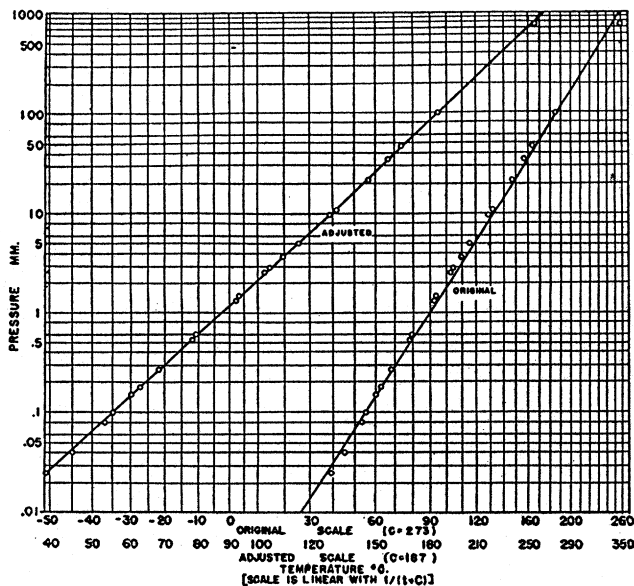(6) Thomson, G. W., *Chem. Rev.*, 38, 1 (1946).